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A.C. Light-emitting Devices Based on Conjugated Polymers

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## AC light-emitting devices based on conjugated polymers

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### Abstract

Most polymer electroluminescent devices to date are represented as tunnel diodes and operate under DC driving field. Here we report the fabrication of symmetrically configured AC light-emitting (SCALE) devices based on conjugated polymers. The new devices consist of an emissive polymer layer sandwiched between two redox polymer layers. This configuration enables the SCALE devices to work under both forward and reverse DC bias as well as in AC modes. The nearly ohmic electrode/redox polymer contacts improve the charge injection efficiency significantly and make the SCALE device operation insensitive to electrode workfunctions. Symmetric operation supports the key role of redox polymer/emissive polymer interface states.

AC electroluminescent devices trace their origin back to 1936 when Destriau discovered electroluminescence (EL) in Cu-doped ZnS phosphors [1]. Although there was a large research effort in the 1950s on AC powder EL devices, such devices never achieved practical application. The existing AC thin film electroluminescent devices [2] based on, for example, Mn-doped ZnS have considerable drawbacks, e.g., high fabrication cost and high operating voltages.

In the past decade, there has been emerging interest in organic molecular [3] and polymeric [4] electroluminescent devices. A variety of organic molecules, conjugated polymers, copolymers, and blends have been found to exhibit electroluminescent properties [5,6]. Light-emitting diodes incorporating these materials have demonstrated all the necessary colors needed for display applications. Extensive research has been devoted to improving device performance. A number of ways have been found to lower the device operating voltage and to increase the quantum efficiency. Multilayer structures [7-9] and low work function cathodes (e.g. Ca [10]) have been introduced to improve charge injection and balance charge transport. However, due to the asymmetry of the device configuration, efficient charge injection generally occurs only in one direction (forward DC bias). Under reverse bias, most of the devices either degrade quickly or show very poor performance. Recently, some materials were found to show EL under reverse DC bias in the simple single-layered structure [11-13]. Also, some multiple bilayer structures prepared by dip coating technique show EL under reverse DC bias [14]. However, these devices show either unstable EL or somewhat asymmetric current-voltage (I-V) characteristics. We report here the fabrication of symmetrically configured AC light-emitting (SCALE) devices based on conjugated polymers. The SCALE devices consist of an active electroluminescent layer sandwiched between two redox polymer layers which are able to accept both electrons and holes. This structure is sandwiched between two conducting electrodes, one of which preferably is transparent. This configuration enables the SCALE devices to work under both forward and reverse DC bias. Due to the relatively fast dynamic response, the devices can also be operated in AC modes. It is suggested that the nearly ohmic behavior of the electrode/redox polymer contact and

the presence of a large density of redox polymer/emissive polymer interface states have a central role in the operation of SCALE devices.

We have fabricated SCALE devices using poly(*p*-pyridine) (PPy) and other electroluminescent polymers such as poly(*p*-pyridyl vinylene) (PPyV) as the emitting materials. Unlike the conventional polymer light-emitting diodes which utilize two dissimilar metals with different work functions as electrodes (one for hole injecting, the other for electron injecting), the contacts for the SCALE device need not be dissimilar metals, as it has been shown that the operation of the SCALE devices is not sensitive to the electrode work functions (see below). This enables utilization of a wide range of contact materials, such as indium-tin-oxide (ITO), aluminum (Al), gold (Au), and highly conducting polyaniline salt.

For the device presented here, PPy was used as the emissive layer; the emeraldine base (EB) form of polyaniline was utilized as the redox material; ITO and Al were used as electrodes. Fig. 1 shows schematically the structure of such SCALE devices.

The syntheses of PPy [15,16] and EB [17] have been reported previously. EB and PPy films were spin-cast from solutions in *N*-methylpyrrolidinone (NMP) and in formic acid, respectively, onto pre-cleaned patterned ITO substrates. The Al electrode was deposited by vacuum evaporation at a pressure of  $\sim 10^{-6}$  torr.

Figure 2 shows the PL spectrum of the PPy film and the absorption spectrum of the EB film. The PL of PPy is peaked at  $\sim 540$  nm (2.3 eV), in the transmission window between the two strong absorptions of EB centered at 327 nm (3.8 eV) and 621 nm (2.0 eV), respectively. The EL spectra of the ITO/EB/PPy/EB/Al device under DC (both forward and reverse) and AC driving voltage are qualitatively similar (see Fig. 2 inset), with almost the same peak position ( $\sim 2.5$  eV or 496 nm) as the single layered ITO/PPy/Al devices reported earlier [15], indicating that the absorption of the EB layer is not significant. Since the present SCALE devices were fabricated and tested in ambient atmosphere and were not optimized, the external quantum efficiency ( $\sim 10^{-4}$  photons/electron) is low. However the quantum efficiency is comparable to or higher than that of the similarly prepared single layer PPy devices [15].

Figure 3 shows the typical I-V characteristics of the SCALE devices. The devices have typical operating voltages of  $\sim 5 - 12$  V, and work equally well under both forward and reverse bias. Under low frequency AC (sinusoidal) driving, light pulses with twice the driving frequency were observed; the time dependent EL intensity of the device driven by a sinusoidal voltage of 60 Hz is shown in Fig. 4. A light pulse is emitted whenever the applied voltage exceeds the positive or negative threshold voltage. The EL intensity is approximately independent of frequency below  $\sim 100$  kHz for devices with active area  $\sim 3$  mm<sup>2</sup> and thickness  $\sim 2000$  Å.

The operating mechanism for the Mn:ZnS thin film EL devices has been explained by the impact ionization of Mn's inner shell produced by hot electrons travelling in the ZnS [2]. These devices do not work in DC bias and EL intensity in AC modes is frequency dependent. Based on the facts that the SCALE device has similar EL spectra in both DC and AC modes and that the EL intensity is nearly independent of frequency for several orders of magnitude, we argue that the mechanism of impact ionization does not apply to the polymer SCALE devices reported here. Whereas the I-V characteristics for most polymer LEDs have been proposed to be controlled by the polymer/metal contacts via work function related mechanisms [18], the symmetric I-V curve under forward and reverse bias for the SCALE devices suggests that the EB/emitter interfaces play a more important role in the SCALE device operation than the EB/electrode interfaces. The argument is supported by the observation that the symmetric I-V characteristics of the SCALE devices are not sensitive to the work functions of the electrodes used. Similar symmetric I-V characteristic was observed (see Fig. 3 inset) when the Al electrode was replaced with gold (Au), which has a much higher work function ( $\sim 5.3$  eV) than Al ( $\sim 4.2$  eV) and even ITO ( $\sim 4.8$  eV) [5]. We point out that although the I-V characteristics are similar for Al and Au electrodes, the current density (at a given voltage) is quite different for the two devices shown.

To study the effects of the EB layer on the device operation, we fabricated devices with different configurations with same PPy thickness: ITO/PPy/Al; ITO/EB/PPy/Al; ITO/PPy/EB/Al; ITO/EB/PPy/EB/Al. All these devices were fabricated and tested un-

der similar conditions. Unusual behavior was observed: the turn on voltage decreases and current density increases as the EB layers were added. This clearly indicates that EB facilitates, instead of limits, the charge injection from the electrodes to the emissive polymer. In fact, symmetric, nearly linear I-V characteristics were observed for ITO/EB/Al sandwich structures, suggesting that very small barriers exist in the EB/electrode interfaces, independent of electrode compositions. Thus, the charge injection barriers have been changed from the electrode/emitter interfaces to the EB/emitter interfaces for the SCALE devices. We believe that this is a significant step in improving the ultimate device characteristics. Due to the expected inter-penetrating network nature of the polymer/polymer interfaces, non-uniform electric fields likely are created making charge injection from the redox polymer to the emissive polymer much easier than from planar metal electrodes directly to the emissive polymer. We note that the non-uniform electric field effects have been clearly demonstrated in PPV devices using high-surface area network conducting polyaniline as a hole injection electrode [19].

It is suggested that the low barrier at the EB/metal contact is due to the unique electronic structure of EB. It is known that negative and positive polaron levels, associated with quinoid and benzenoid levels respectively, exist within the  $\pi$ - $\pi^*$  band gap of EB. These localized polaron levels can accept electrons (or holes) easily to vary its oxidation states reversibly. We note that while ITO/EB/PPy/EB/Al and ITO/EB/PPy/Al devices emit light in both forward and reverse bias, no light (or very weak light) was observed for ITO/PPy/Al and ITO/PPy/EB/Al devices under reverse bias, indicating that electron injection from ITO to PPy is the main efficiency limiting step in the device operation under reverse bias.

We propose the following mechanism for the polymer SCALE device operation: Under low bias voltage, the charge carriers are injected through essentially ohmic contacts from the electrodes into the polaron levels of the EB layers, regardless of initial polarity of the applied voltage. The injected charges transport to the EB/emitter interfaces via a hopping mechanism and populate the EB/emitter interfaces. When the applied electric field is high enough, the accumulated charges begin to inject into the emissive layer from the interfaces.

The injected charges may form intrachain excitons and decay radiatively to emit light or follow other nonradiative decay paths. A portion of the injected charges may migrate through the emissive layer without decaying. Most of these charges will be trapped in the opposite emitter/EB interface. When the bias voltage is reversed, the shallow trapped charges will be released from the interfaces and contribute to the recombination current. The deep trapped charges which act as quenchers or injection limiters will be neutralized. The electrochemical reactions that occur at the interfaces may be partially reversed when the bias is changed, making the SCALE devices more stable when operating in AC modes. We note that the present devices work better under low frequencies ( $\leq 100$  kHz) because of the capacitance effects created by the device structure. At high frequencies, the injected charges cannot follow the electric field, and the EL intensity decreases dramatically.

Although the present SCALE devices have not yet been optimized for efficiency, a number of potentially important advantages over the "conventional" polymer LEDs are already apparent:

(1) The limiting barriers for charge injection are moved from the electrode/polymer interfaces (where the barriers are difficult to reduce and control) to the redox polymer/emissive polymer interfaces, which dramatically reduces the overall charge injection barriers thereby lowering operating voltages, and allows control using a full range of organic/polymer chemistry. This could lead to significant improvement in charge injection efficiency by choosing appropriate redox polymers.

(2) Because the charge injection from the electrodes to the redox polymer is nearly ohmic for a variety of metals, the SCALE device performance is not sensitive to the electrodes used. This enables the use of stable high work function metals (including gold) as both electrodes, potentially reducing the aging problems associated with "conventional" polymer LEDs which must use reactive low work function metals to achieve efficient electron injection.

(3) The SCALE devices can operate equally well under both forward and reverse DC bias. The relatively fast dynamic response enables the device operation in AC modes. Be-

cause the electrochemical reactions that occur at the interfaces may be partially reversed when the bias is changed, a longer lifetime is expected when the devices operate in AC modes.

The concept of the symmetrically structured polymer light-emitting devices reported here is quite general [20]. As suggested by the important roles played by the polymer-polymer interfaces in the device operation, this concept can be applied to a variety of electroluminescent polymers in conjunction with suitable polymers to fabricate SCALE devices.

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- [20] We have successfully replaced the two layers of the redox polymer EB with two much thinner layers of insulating polymer polymethylmethacrylate (PMMA) although these SCALE devices have somewhat lower efficiencies. Tunneling from electrode contacts through PMMA to PMMA/emissive polymer interface states likely occurs in this configuration.

## FIGURES

FIG. 1. Schematic diagram of the structure of a SCALE device using PPy as the emitting material and EB as the insulating redox material.

FIG. 2. Absorption spectrum of EB film cast from NMP solution compared with photoluminescence (PL) spectrum of PPy film cast from formic acid solution. To simulate the device fabrication process, the EB film was "spin-coated" with formic acid which partially doped the EB. The PL spectrum was taken with 351 nm excitation. Inset: electroluminescence spectrum for a SCALE device ITO/EB/PPy/EB/Al under (a) DC forward bias, (b) DC reverse bias, and (c) AC driving voltage (60 Hz sinusoidal). Spectra are offset for clarity.

FIG. 3. Current-voltage characteristic for a SCALE device ITO/EB/PPy/EB/Al device under forward and reverse DC bias. The EB layers ( $\sim 500$  Å each) are spin coated from NMP solution, and the PPy layer ( $\sim 1000$  Å) is spin coated from formic acid solution. The active area of the device is  $\sim 3$  mm<sup>2</sup>. Inset: I-V characteristic for a SCALE device ITO/EB/PPy/EB/Al under forward and reverse DC bias.

FIG. 4. Electroluminescence intensity as a function of time for a SCALE device ITO/EB/PPy/EB/Al driven by a 60 Hz sinusoidal voltage.

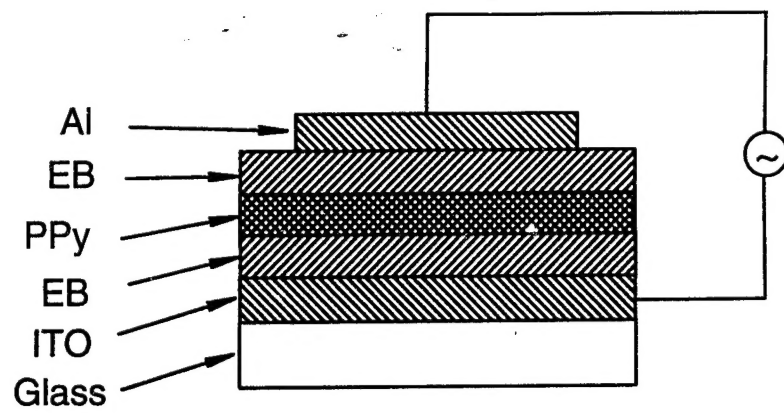


Fig. 1 Wang *et al.*

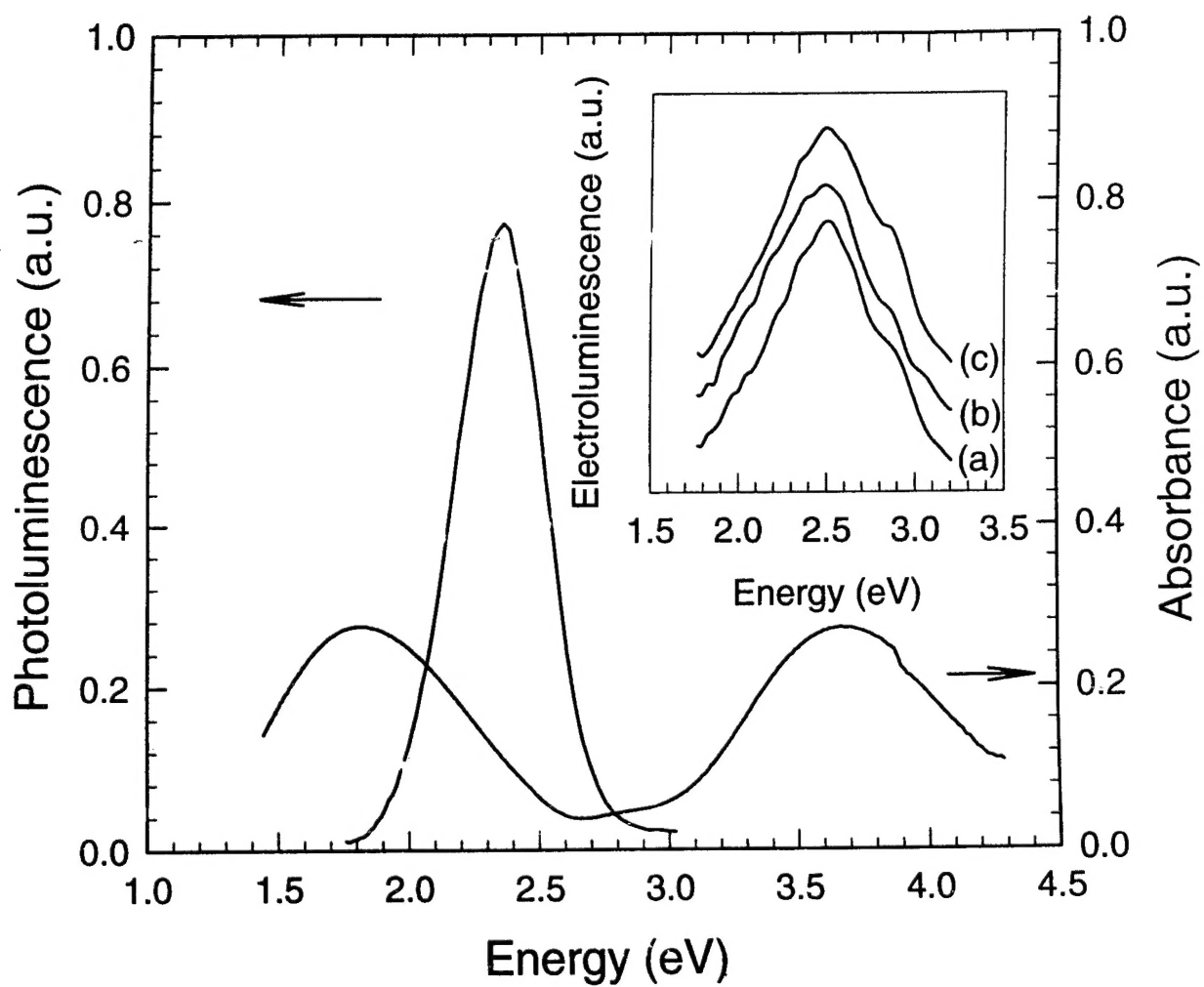


Fig. 2 Wang *et al.*

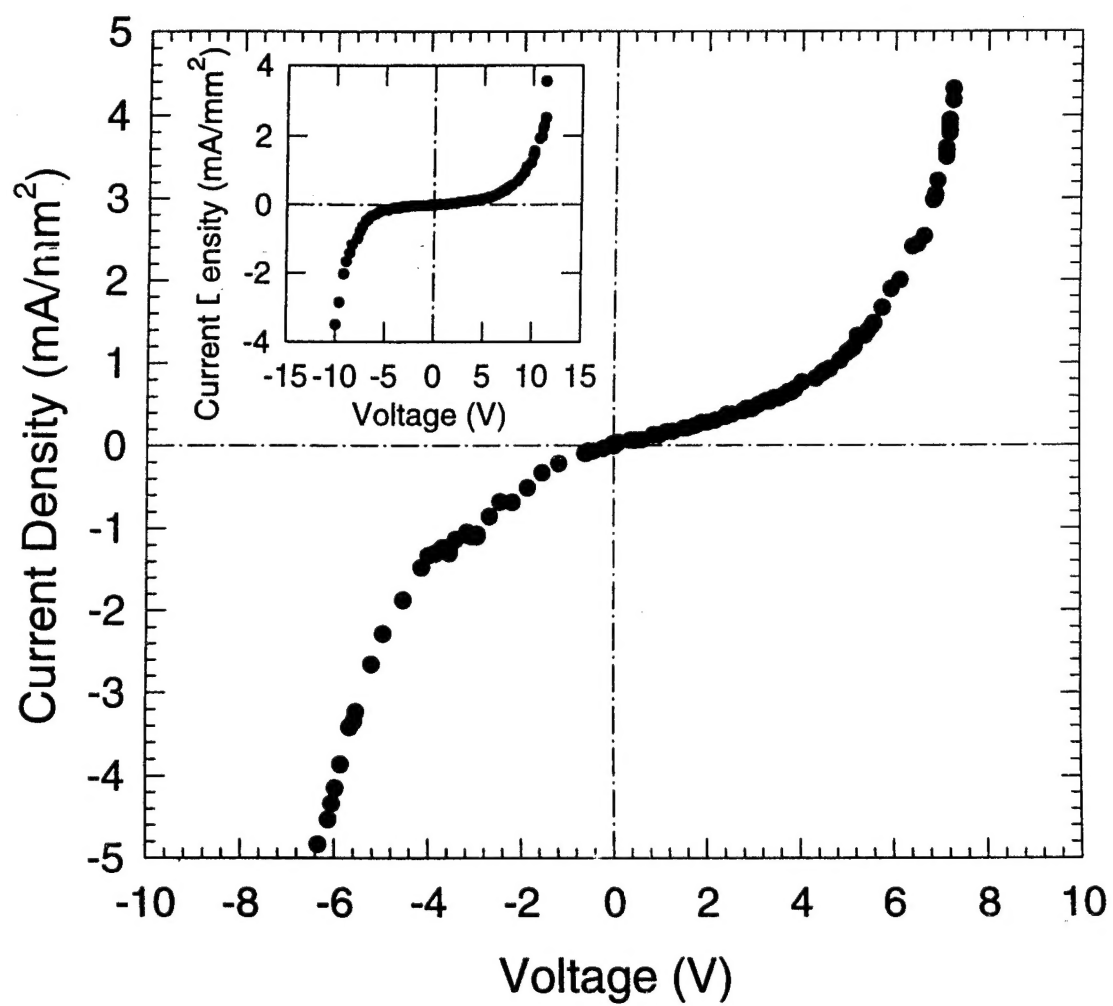


Fig. 3 Wang *et al.*

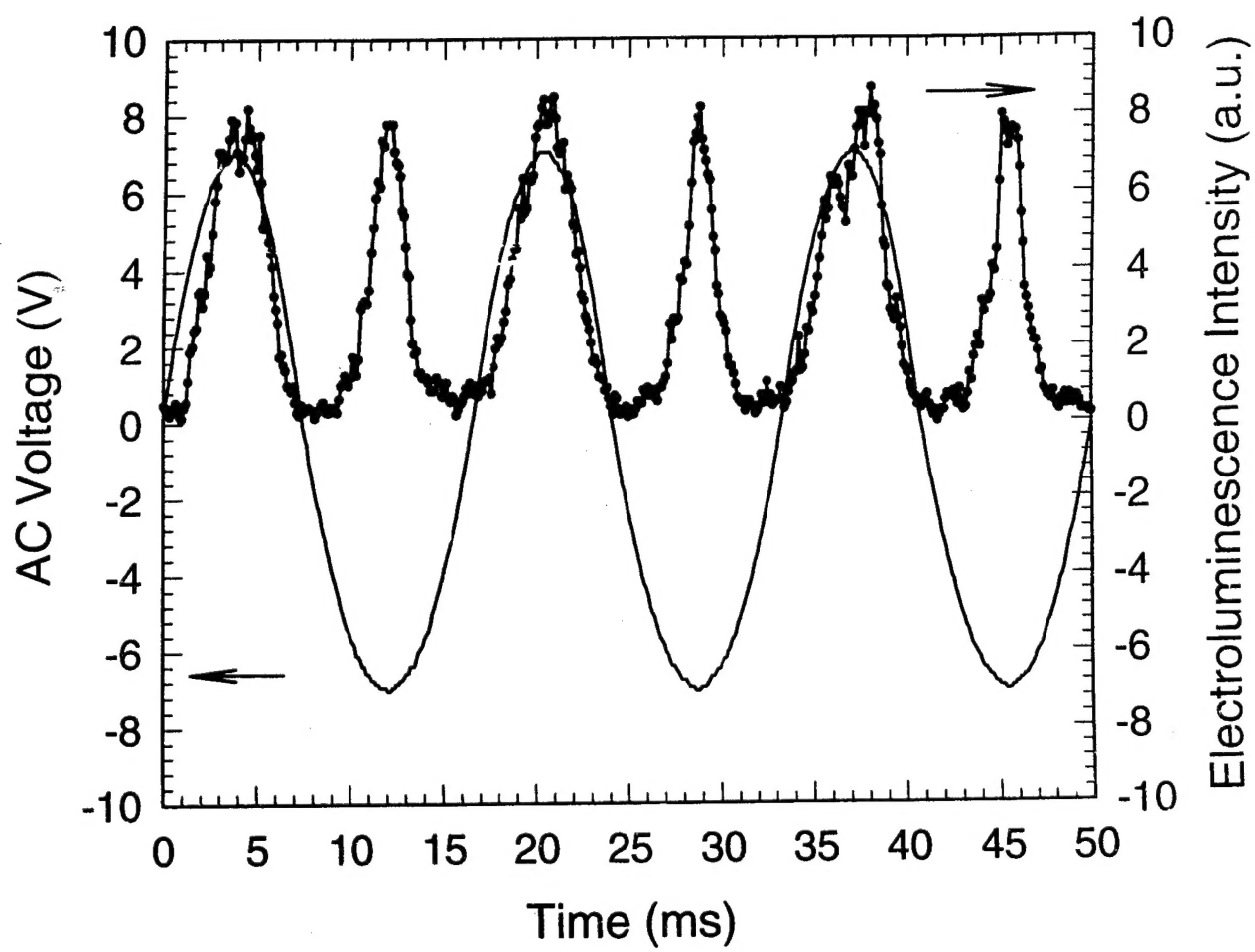


Fig. 4 Wang *et al.*